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File: USPT

Oct 13, 1987

DOCUMENT-IDENTIFIER: US 4699857 A  
TITLE: Battery separator

Abstract Text (1):

A battery separator in the form of a microporous membrane composed of a substantially uniform composition of a polymer mixture of ultra high molecular weight polyolefin, polyethylene terpolymer and polyvinyl chloride, in combination with at least one plasticizer for the polymer mixture and an inert filler.

Brief Summary Text (5):

The separator is preferably in the form of a diaphragm or envelope (in which an electrode of at least one polarity is encased) which is microporous and has a high void volume. Such configurations permit the necessary free flow of electrolytic conductivity (low resistivity) while inhibiting active materials from passing through the separator causing unwanted bridging of plates of opposite polarity. Such contact may be due to imperfections in the plate structure or due to dendrite growth on the electrode during use or the like.

Brief Summary Text (6):

In addition to the above requirements the separator must be capable of being formed into a very thin sheet which is substantially inert to the environment established by the battery system. For example, it is well known that the battery forms an oxidative environment which causes degradation of materials used in forming conventional separators which, in turn, causes disintegration of the thin separator membrane. The ability to produce a separator membrane which is capable of withstanding the oxidative forces of the battery environment while fulfilling the other criteria of being microporous, having a high void volume, having a very thin cross-section, being inert to the battery components, exhibiting low electrical resistivity, and exhibiting high resistivity to passage of active material is highly desired.

Brief Summary Text (9):

U.S. Pat. No. 4,287,276 is directed to the formation of a battery separator specifically useful in alkaline battery systems. The polyolefin matrix is highly filled with a particular class of fillers to form a microporous sheet having enhanced resistance to dendrite formation.

Brief Summary Text (13):

The present separator is a microporous membrane composed of a substantially homogeneous composition of (a) a polymer mixture formed from a polyolefin having a weight average molecular weight of at least 3 million, a partially crosslinked ethylene terpolymer and a vinyl or vinylidene halide polymer; (b) an inert filler and (c) a plasticizer for at least one of the polymer components.

Brief Summary Text (15):

The battery separator of the present invention is in the form of a very thin membrane or sheet which is formed from a substantially homogeneous mixture of a polymer blend, an inert filler and a plasticizer. Each of the components is fully described hereinbelow.

Brief Summary Text (21):

The ethylene terpolymer in the compatible blend is partially crosslinked. This can be carried out using any one or more of the well known crosslinking techniques including electron beam irradiation, gamma irradiation and free radical curatives such as peroxides. The crosslinking of the ethylene copolymer according to this invention can

be carried out before or concurrently with blending with the vinyl or vinylidene halide polymers, or after such blending when using radiation techniques to effectuate the crosslinking. If the ethylene terpolymer in the blend contains carbon monoxide, diamines such as methylene dianiline or p-phenylene diamine can be used to effectuate the desired crosslinking. If the ethylene terpolymer is ethylene/vinyl acetate/carbon monoxide, sulfur vulcanizing agents can be used as detailed in U.S. Pat. No. 4,172,939. For crosslinking ethylene terpolymers containing carboxylic acid functionalities, the formation of ionic crosslinks is suitable in the practice of the subject invention, and is achieved with various metal oxides or hydroxides such as ZnO and NaOH, or with organometallics such as chromium acetylacetonate, as detailed in U.S. Pat. No. 4,304,887.

Brief Summary Text (25):

The plasticizer of the instant composition further improves the processability of the composition, i.e., lower the melt viscosity, or reduces the amount of power input which is required to compound and to fabricate the composition and aids in inducing porosity, as discussed hereinbelow. The microporous separator of the present invention is formed from an initial composition having a very high content of plasticizer therein, such as, at least about 30 vol. percent and preferably at least 50 vol. percent based on the initial composition.

Brief Summary Text (29):

The term "sheet" or "membrane" as used in the subject application is intended to define a substantially planar material which is formed from the initially composed admixture both prior and subsequent to extraction of plasticizer therefrom. The sheet material should be preferably, a film which is less than about 20 mils thick and more preferably, less than 10 mils thick with from about 2 to 7 being most preferred. It has been found that the highly filled polymeric composition of the present invention can be readily formed into such thin sheet material by conventional techniques. Separators formed from the sheet can be used in their planar form between electrodes of opposite polarity or can be formed into other configurations, such as pocket or envelopes, of suitable size to encase an electrode and provide separation between electrode pairs.

Brief Summary Text (32):

Examples of material which are suitable as fillers in appropriate application include materials which are soluble or insoluble in water. Representative of the fillers which are substantially water insoluble and operable in the instant invention are carbon black, coal dust and graphite; metal oxides and hydroxides such as those of silicon, aluminum, calcium, magnesium, barium, titanium, iron, zinc, and tin; metal carbonates such as those of calcium and magnesium; minerals such as mica, montmorillonite, kaolinite, attapulgite, asbestos, talc, diatomaceous earth and vermiculite; synthetic and natural zeolites; portland cement; precipitated metal silicates such as calcium silicate and aluminum polysilicate; alumina silica gels; wood flour, wood fibers and bark products; glass particles including microbeads, hollow microspheres, flakes and fibers.

Brief Summary Text (38):

The composition of the resultant separator will depend upon the degree of extraction of the plasticizer. The plasticizer can be substantially completely removed, leaving a highly filled polymeric sheet product or, alternatively, can have 60 percent and, preferably, 75 percent of the plasticizer of the admixture removed. These products normally show good retention of physical properties, as well as good electrical stability. The extracted separator membrane normally has from about 7 to 50 percent of the polymer mixture about 50 to 93 percent filler, and from about 0 to 20 percent plasticizer. The more preferred separators comprise a mixture of from 10 to 25 percent polymer mixture, 60 to 90 percent filler, and from 2 to 15 percent plasticizer.

Brief Summary Text (43):

When the separator is to be provided with rib members (such as for use in an acid battery) these members can be formed from the same composition or from other polymeric compositions which are compatible with the present composition. For example, other polymer compositions can be filled, unfilled or foamed polyolefins, polyvinyl chloride and the like. Alternately, the separator sheet can be grooved or embossed to provide the channel members to permit egress of gaseous products from the battery system. Other similar modifications can be made in known manners. The instant process and composition produce microporous battery separators which exhibit low electrical resistance, readily permits electrical conductivity via the electrolyte, and possess excellent tensile properties to accommodate the various physical forces encountered in the battery during operation. In addition, the present separator exhibits a high degree of stability and

lack of degradation to the various chemical and electrochemical forces encountered in the battery.

Detailed Description Text (4):

The compounded composition was pressed into sheets of approximately 10 mils thickness using a hydraulic press with heated plates (150.degree. C.) at a pressure of 3000 psi. The formed sheets were observed to be a cohesive flexible material which was suitable for further handling and processing. The sheets were immersed in a bath of hexane maintained at ambient temperature for 15 minutes to extract out the petroleum oil and then dried. The extracted materials were microporous sheets having cross-sectional thickness of 10 mils and a void volume of about 73 volume percent. The highly filled sheets were composed of 34.2 percent polymer and 65.8 percent silica.

Detailed Description Text (8):

A separator membrane was formed in the same manner as described in Example I above except that 6.6 parts (6.9 vol. percent) of polyethylene of 5,000,000 weight average molecular weight and 8.6 parts (6.9 vol. percent) of the polymer blend used in Example I above (Alcryn--80A) were used to form the composition. The torque required for mixing the composition was measured to be 100 gram .multidot. meters. The extracted sheet had a thickness of 10 mils. The sample was tested in the same manner as described in Example 1. The results are shown in Table II below.

Detailed Description Text (14):

The above results show that although the samples are microporous and exhibit the desired low electrical resistance, they each severely deteriorate due to oxidation. In each case the material became brittle, would be easily damaged due to the forces exerted on a separator during use and would thereby permit shortening of the battery life.

Detailed Description Text (17):

The above results shows that the formed microporous sheet exhibits high electrical resistance and poor oxidation stability.

CLAIMS:

1. In a battery system composed of at least one pair of electrodes of opposite polarity, an electrolyte and a separator positioned between electrodes of opposite polarity, the improvement comprising that said separator is a microporous sheet composed of a substantially uniform composition of

A. from 7 to 50 weight percent of a polymer mixture, said mixture formed from

(a) from about 95 to about 40 weight percent of polyolefin formed from ethylene, propylene or mixtures thereof or a mixture of said polyolefins having a weight average molecular weight of at least about 3,000,000; and

(b) from about 5 to about 60 weight percent of a polymeric blend formed from a polyethylene terpolymer and a vinyl or vinylidene halide polymer in a weight ratio of 19:1 to 1:3, said polyethylene terpolymer formed from (1) ethylene monomer, (2) at least one ethylenically unsaturated organic monomer selected from the group consisting of esters of unsaturated C.sub.3 -C.sub.20 mono- or dicarboxylic acids, vinyl esters of saturated C.sub.2 -C.sub.18 carboxylic acids, vinyl alkyl ethers wherein the alkyl group has 1-18 carbon atoms, vinyl or vinylidene halides, acrylonitrile, methacrylonitrile, norbornene, alpha-olefins of 3-12 carbon atoms, and vinyl aromatic compounds, and, (3) an additional monomer selected from the group consisting of ethylenically unsaturated C.sub.3 -C.sub.20 carboxylic acids, carbon monoxide, and sulfur dioxide;

B. from 93 to 50 weight percent of a filler which is substantially inert with respect to the battery electrodes and electrolyte; and

C. from 0 to 20 weight percent of plasticizer for at least one of said polymers of the composition.

20. In a battery system composed of at least one pair of electrodes of opposite polarity, an electrolyte and a separator positioned between electrodes of opposite polarity, the improvement comprising that said separator is a microporous sheet composed of a substantially uniform composition of

A. from 7 to 50 weight percent of a polymer mixture, said mixture formed from

(a) from about 95 to about 40 weight percent of polyolefin formed from ethylene, propylene or mixtures thereof or a mixture of said polyolefins having a weight average molecular weight of at least about 3,000,000; and

(b) from about 5 to about 60 weight percent of a polyethylene terpolymer formed from (1) ethylene monomer, (2) at least one ethylenically unsaturated organic monomer selected from the group consisting of esters of unsaturated C.sub.3 -C.sub.20 mono- or dicarboxylic acids, vinyl esters of saturated C.sub.2 -C.sub.18 carboxylic acids, vinyl alkyl ethers wherein the alkyl group has 1-18 carbon atoms, vinyl or vinylidene halides, acrylonitrile, methacrylonitrile, norbornene, alpha-olefins of 3-12 carbon atoms, and vinyl aromatic compounds, and, (3) an additional monomer selected from the group consisting of carbon monoxide, and sulfur dioxide;

B. from 93 to 50 weight percent of a filler which is substantially inert with respect to the battery electrodes and electrolyte; and

C. from 0 to 20 weight percent of plasticizer for at least one of said polymers of the composition.

22. A separator sheet product comprising a microporous sheet having a thickness of less than about 20 mils composed of a substantially uniform composition of

(A) from 7 to 50 weight percent of a polymer mixture, said mixture formed from

(a) from about 95 to about 40 weight percent of polyolefin formed from ethylene, propylene or mixtures thereof or a mixture of said polyolefins having a weight average molecular weight of at least about 3,000,000; and

(b) from about 5 to about 60 weight percent of polymeric blend formed from a polyethylene terpolymer and a vinyl or vinylidene halide polymer in a weight ratio of 19:1 to 1:3, said polyethylene terpolymer formed from (1) ethylene monomer, (2) at least one ethylenically unsaturated organic monomer selected from the group consisting of esters of unsaturated C.sub.3 -C.sub.20 mono- or dicarboxylic acids, vinyl esters of saturated C.sub.2 -C.sub.18 carboxylic acids, vinyl alkyl ethers wherein the alkyl group has 1-18 carbon atoms, vinyl or vinylidene halides, acrylonitrile, methacrylonitrile, norbornene, alpha olefins of 3-12 carbon atoms, and vinyl aromatic compounds, and, (3) an additional monomer selected from the group consisting of ethylenically unsaturated C.sub.3 -C.sub.20 carboxylic acids, carbon monoxide, and sulfur dioxide;

B. from 93 to 50 weight percent of a filler which is substantially inert with respect to the battery electrodes and electrolyte; and

C. from 0 to 20 weight percent of plasticizer for at least one of said polymers of the composition

24. A separator sheet product comprising a microporous sheet having a thickness of less than about 20 mils composed of a substantially uniform composition of

(A) from 7 to 50 weight percent of a polymer mixture, said mixture formed from

(a) from about 95 to about 40 weight percent of polyolefin formed from ethylene, propylene or mixtures thereof or a mixture of said polyolefins having a weight average molecular weight of at least about 3,000,000; and

(b) from about 5 to about 60 weight percent of a polyethylene terpolymer formed from (1) ethylene monomer, (2) at least one ethylenically unsaturated organic monomer selected from the group consisting of esters of unsaturated C.sub.3 -C.sub.20 mono- or dicarboxylic acids, vinyl esters of saturated C.sub.2 -C.sub.18 carboxylic acids, vinyl alkyl ethers wherein the alkyl group has 1-18 carbon atoms, vinyl or vinylidene halides, acrylonitrile, methacrylonitrile, norbornene, alpha olefins of 3-12 carbon atoms, and vinyl aromatic compounds, and, (3) an additional monomer selected from the group consisting of carbon monoxide, and sulfur dioxide;

B. from 93 to 50 weight percent of a filler which is substantially inert with respect to the battery electrodes and electrolyte; and

C. from 0 to 20 weight percent of plasticizer for at least one of said polymers of the composition.

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END OF SEARCH HISTORY